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(54) Title: PROCESS FOR PRODUCING N-METHYLATED ORGANIC PIGMENTS			
(57) Abstract <p>A process for producing an organic pigment represented by the general formula (I): $A(H)_x(CH_3)_y$, characterized in that an organic pigment represented by the formula (II): $A(H)_{x+y}$, is reacted with dimethylcarbonate in the presence of a base with or without a solvent, wherein in formulae (I and II) $x + y$ is an integer 1 to 4 with x being 0 to 4 and y being 1 to 4, A is the residue of an organic pigment containing $x + y$ cyclic or open -NH- groups, and the H as well as CH_3 in formula (I and II) are bound to the above mentioned N. This process is suitable for the production of N-methylated organic pigments in an environmentally safe process and at a low production cost.</p>			

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- 1 -

Process for producing N-methylated organic pigments

The present invention relates to a process for the production of N-methylated organic pigments.

Some N-methylated organic pigments are known in the art. For example, N,N'-dimethyl-substituted pyrrolo[3,4-c]pyrroles are described in US Patent 4,585,878; N,N'-dimethyl-quinacridone is reported by L. L. Pushkina et al in Zh. Org. Khim. 20, 1939(1984); N,N'-dimethyl-substituted perylenedicarboxylic acid diimide is disclosed in US Patent 3,673,192; N,N'-dimethyl-indigo is described by G. A. Russel et al in J. Am. Chem. Soc., 91, 3851(1969).

These compounds are used especially as coloring agents for polymeric materials. The processes for the production of these compounds involve without exception the N-methylation step using methyl iodide or dimethyl sulfate as methylating agents.

However, the above mentioned methylating agents are of high toxicity, so that particular care must be exercised during the N-methylation process. Moreover, methyl iodide and dimethyl sulfate are expensive reagents. Accordingly, the prior art method for the N-methylation of organic pigments has drawbacks in that it can cause problems with respect to environmental protection and that the production cost of the N-methylated organic pigments are high.

It is therefore desirable that an alternative process be developed which is environmentally safe and which enables the production of N-methylated organic pigments at a low production cost.

On the other hand, it is described in M. Lissel et al, Synthesis, 382, (1986) that imidazole can be methylated in good yield by using dimethyl carbonate under phase transfer conditions.

However, M. Lissel et al neither disclose nor suggest that insoluble organic pigments can,

- 2 -

surprisingly, be N-methylated in suspensions in good yield by using dimethyl carbonate and a base but without using a phase transfer catalysts, thereby enabling the production of N-methylated organic pigments at a low production cost in an environmentally safe process.

Accordingly, the present invention relates to a process for producing an organic pigment represented by general formula



characterized in that an organic pigment represented by formula

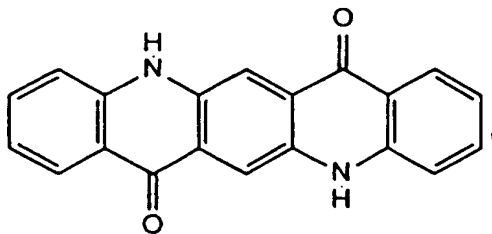


is reacted with dimethylcarbonate in the presence of a base with or without a solvent, wherein in formulae I and II $x + y$ is an integer 1 to 4 with x being 0 to 4 and y being 1 to 4, A is the residue of an organic pigment containing $x + y$ cyclic or open -NH- groups, and the H as well as CH_3 in formula I and II are bound to the above mentioned N.

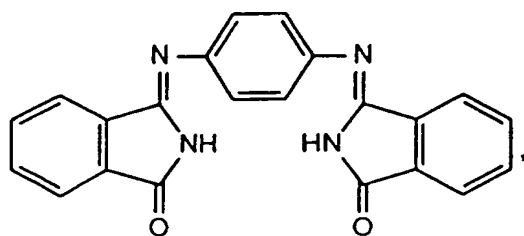
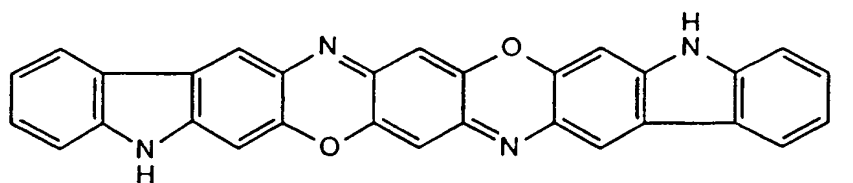
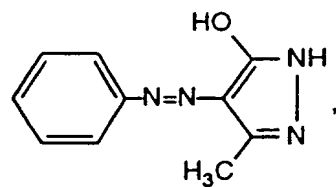
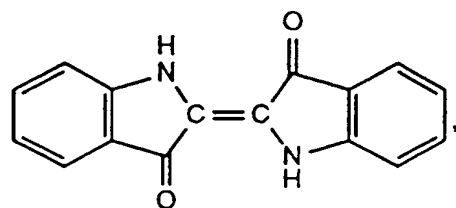
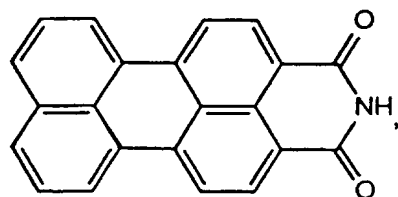
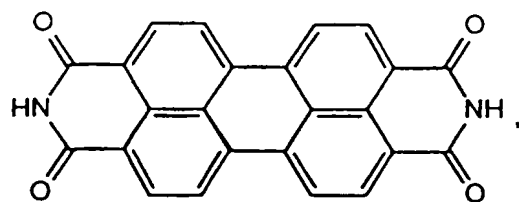
$x + y$ is preferably 1 or 2.

A in formulae I and II is preferably the residue of a pigment selected from the group consisting of the quinacridone, anthraquinone, perylene, indigo, quinophthalone, isoindolinone, isoindoline, dioxazine, diketopyrrolopyrrole, phthalocyanine or azo series.

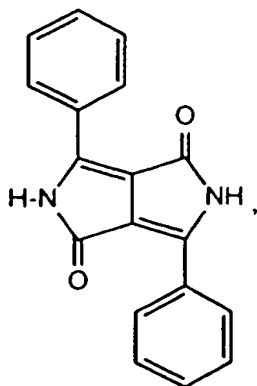
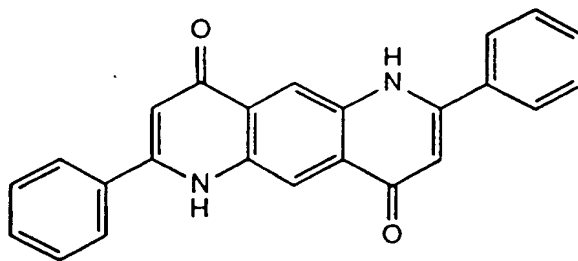
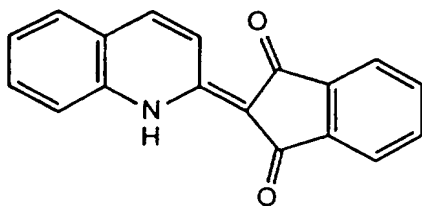
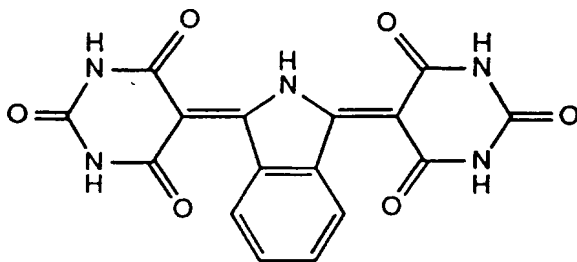
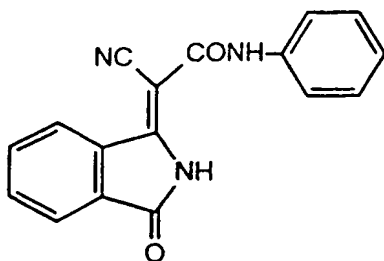
Examples of such organic pigments include:



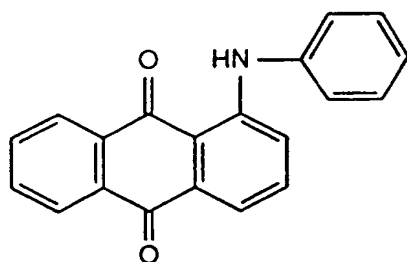
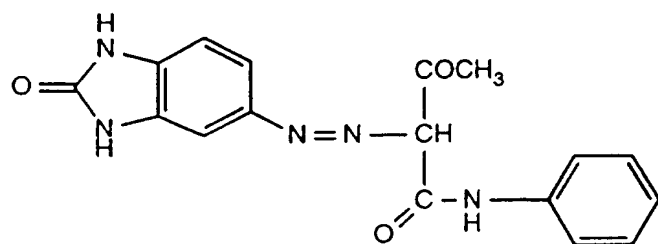
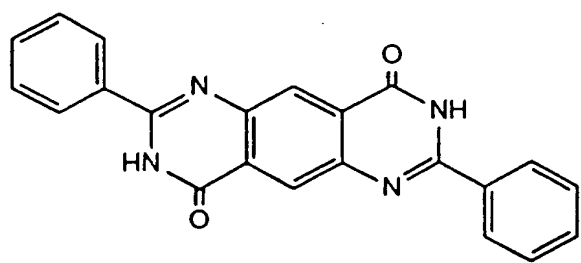
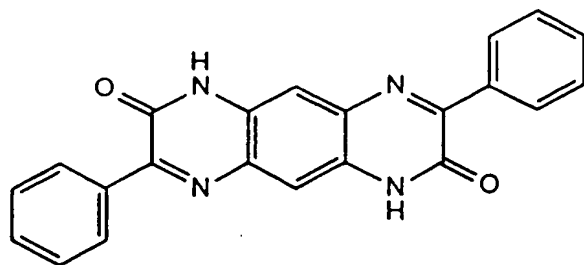
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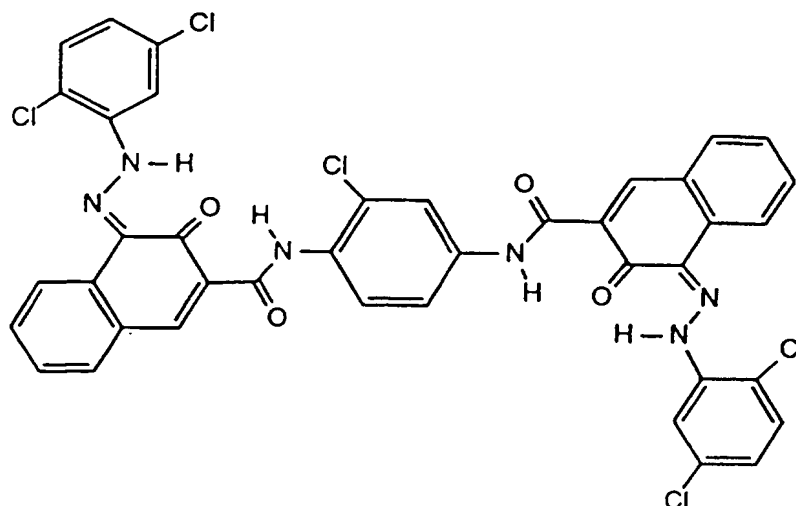
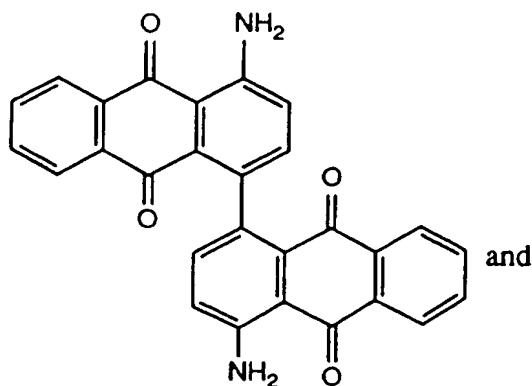
- 4 -



- 5 -



- 6 -



as well as all the known derivatives of the above chromophores.

The bases eligible for use in the process of the instant invention are, for example, the alkaline metals themselves, such as lithium, sodium or potassium as well as their hydroxides and carbonates, or alkaline metal amides, such as lithium, sodium or potassium amide or alkaline metal hydrides, such as lithium, sodium or potassium hydride, or alkaline earth or alkaline metal alcoholates, which are derived especially from primary, secondary or tertiary aliphatic alcohols with 1 to 10 C-atoms, e.g., lithium, sodium or potassium methylate, ethylate, n-propylate, isopropylate, n-butylate, sec.-butylate, tert.-butylate, 2-methyl-2-butylate, 2-methyl-2-pentylate, 3-methyl-3-pentylate, 3-ethyl-3-pentylate, and further, preferably, organic aliphatic, aromatic or heterocyclic N-bases, especially, for example, diazabicyclooctene, diazabicycloundecene, trialkylamines, such as trimethyl- or triethylamine, pyridine and substituted pyridines, such as 4-dimethylaminopyridine. The above bases can be used also as mixtures.

- 7 -

Especially preferred bases are, for example, organic aliphatic, aromatic or heterocyclic N-bases, particularly, trimethylamine, triethylamine, pyridine and 4-dimethylaminopyridine.

In the instant invention, the reaction can be accomplished with or without using a solvent. When solvents are to be used, polar organic solvents are preferred. Examples of such solvents are ethers, such as tetrahydrofuran or dioxane, or glycol ethers, such as ethylene glycol methyl ether, ethylene glycol ethylether, acetonitrile, benzonitrile, N,N-dimethylformamide, N,N-dimethylacetamide, nitrobenzene, N-methylpyrrolidone, halogenated aliphatic or aromatic hydrocarbons, such as trichloroethane, benzene or benzene substituted by alkyl, alkoxy or halogen, e.g., toluene, xylene, anisole or chlorobenzene, or aromatic N-heterocycles, such as pyridine, picoline or quinoline. These solvents can be used also as mixtures.

Especially preferred solvents are, for example, tetrahydrofuran, N,N-dimethylformamide, dioxane, dimethylsulfoxide, N,N-dimethylacetamide or N-methylpyrrolidone.

The reaction of the instant invention is carried out by simply mixing the compound represented by formula II, dimethylcarbonate and a base, with or without a solvent, and stirring the thus prepared mixture.

When no solvent is used, the compound of formula II, the base and dimethylcarbonate are mixed in a molar ratio of 1 : 0.1-1000 : 1-100000, preferably 1 : 1-100 : 10-10000, more preferably 1 : 1-50 : 10-1000 and most preferably 1 : 1-10 : 10-500. In this case, the dimethylcarbonate acts as a N-methylating agent as well as a reaction solvent. If a solvent is to be used, the compound of formula II, the base and dimethylcarbonate are added to the solvent such that their molar ratio is 1 : 0.1-100 : 0.1-100, preferably 1 : 1-50 : 1-50, more preferably 1 : 1-20 : 1-20 and most preferably 1 : 1-10 : 1-10. The solvent is used such that the concentration of the compound of formula II is 0.00001-100 mol/l, preferably 0.001-10 mol/l, more preferably 0.01-1 mol/l and most preferably 0.05-0.5 mol/l.

The reaction is carried out in air or in an inert atmosphere. Preferably, it is accomplished in an inert atmosphere such as for example under nitrogen gas, argon or helium. A nitrogen atmosphere is especially preferred.

- 8 -

The pressure under which the reaction is carried out may be varied within the range of from ambient pressure to a high pressure e.g. 500 atm. But, from the viewpoint of ease in operation, ambient pressure is especially preferred.

The reaction temperature is preferably 30-250°C, more preferably 50-200°C and most preferred 80-150°C.

The reaction is accomplished preferably for 1-100 hours, more preferably 2-80 hours and most preferably 2-50 hours.

The resulting compound of formula I is usually a mixture of compounds with a different degree of N-methylation. The longer the reaction time, the higher the yield in compounds of formula I with higher degree of N-methylation if $x + y$ is equal to or larger than 2. Therefore, if it is desired to separate the components with different degree of N-methylation, the reaction mixture after reaction is subjected to a separation process. Any conventional separation method, such as one in which the difference in solubility in a solvent is used or a one in which a separating column is used, can be applied for this purpose. However, the separation using a column is especially preferred. Most preferably, the reaction product is separated by silica gel column chromatography using a non-polar or polar organic solvent e.g. hexane, dichloromethane or ethyl acetate. Suitable conditions for silica gel column chromatography are well known in the art.

In the process according to the instant invention, the compound represented by formula I is obtained in a yield of up to 92 %.

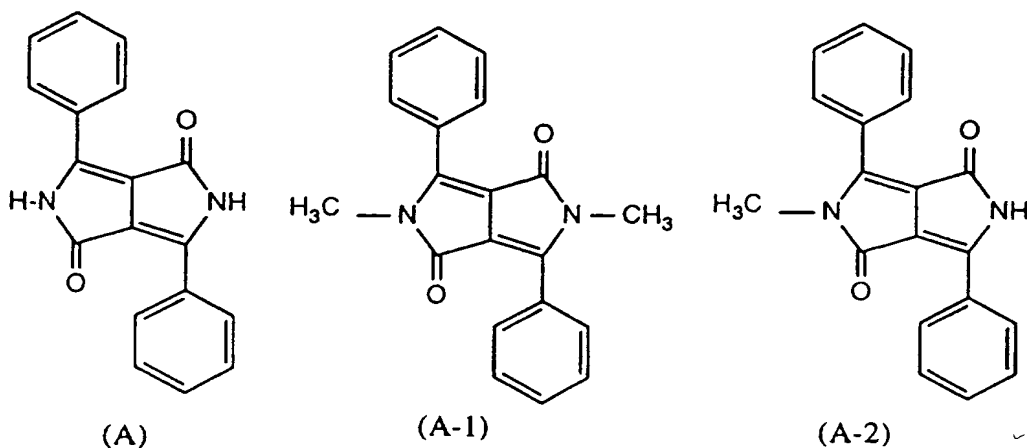
As described above, the present process makes it possible to prepare N-methylated organic pigments easily and at a high production yield without using toxic and expensive compounds such as methyl iodide or dimethyl sulfate. Therefore, the process of the invention is environmentally very safe and economical.

Examples

Example 1

A solution of 0.7 g (6.92 mmol) of triethylamine in 5 ml of dimethyl acetamide (hereinafter, referred to as DMA) is added to a suspension of 0.5 g (1.73 mmol) of 1,4-diketo-pyrrolo[3,4-c]-pyrrole as indicated by A below in 25 ml of DMA, to which

0.374 g (4.15 mmol) of dimethyl carbonate are further added. The suspension is heated to 110°C and stirred for 48 hours at said temperature under N₂ atmosphere. The reaction system is then mixed with 100 ml water, and the mixture is subjected to extraction using dichloromethane. The organic phase is washed with water, dried over magnesium sulfate and subsequently concentrated under vacuum. The residue (0.49 g) is chromatographed on a silica gel column using a solvent mixture consisting of 83 vol% dichloromethane and 17 vol% ethyl acetate. The first yellow-orange zone yields 315 mg of a compound A-1, and the second orange-yellow zone yields 151 mg of a compound A-2. NMR, mass spectroscopic and elementary analyses reveal that these compounds A-1 and A-2 are respectively N,N'-dimethyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole as indicated by A-1 and N-methyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole as indicated by A-2. The yield of A-1 is 46 %, while that of A-2 is 23 %.



Analytical data:

For A-1:

¹H NMR (CDCl₃): 7.89 (m, 4H, Ar-H), 7.54 (m, 6H, Ar-H), 3.34 (s, 6H, N-CH₃).

Mass spectrometry (*m/e*): 316 (M⁺, 100 %).

Elemental analysis (%): C, 75.94; H, 5.06; N, 8.86 (calculated) and C, 75.88; H, 5.22; N, 8.78 (observed).

For A-2:

¹H NMR (CDCl₃): 9.05 (s, br, 1H, N-H), 8.31 (m, 2H, Ar-H), 7.92 (m, 2H, Ar-H), 7.54

- 10 -

(m, 6H, Ar-*H*), 3.41 (s, 3H, N-*CH*₃).

Mass spectrometry (*m/e*): 302 (*M*⁺, 100 %).

Elemental analysis (%): C, 75.49; H, 4.63; N, 9.27 (calculated) and C, 75.43; H, 5.83; N, 9.09 (found).

Example 2

2.9 ml (20.82 mmol) of triethylamine are added to a suspension of 0.5 g (1.73 mmol) of 1,4-diketo-pyrrolo[3,4-*c*]-pyrrole in 30 ml of dimethyl carbonate, which mixture is heated under reflux condition for 96 hours in a nitrogenic atmosphere. The resulting red-brown solution is concentrated under vacuum, and the residue is suspended in ethanol. The precipitate thereby formed is filtered and dried. NMR, mass spectroscopic and elemental analyses reveal that the red-brown crystalline product is N,N'-dimethyl-1,4-diketo-pyrrolo[3,4-*c*]-pyrrole. The yield is 0.25 g, which corresponds to 45.7 % in yield.

Analytical data:

¹H NMR (CDCl₃): 7.89 (m, 4H, Ar-*H*), 7.54 (m, 6H, Ar-*H*), 3.34 (s, 6H, N-*CH*₃).

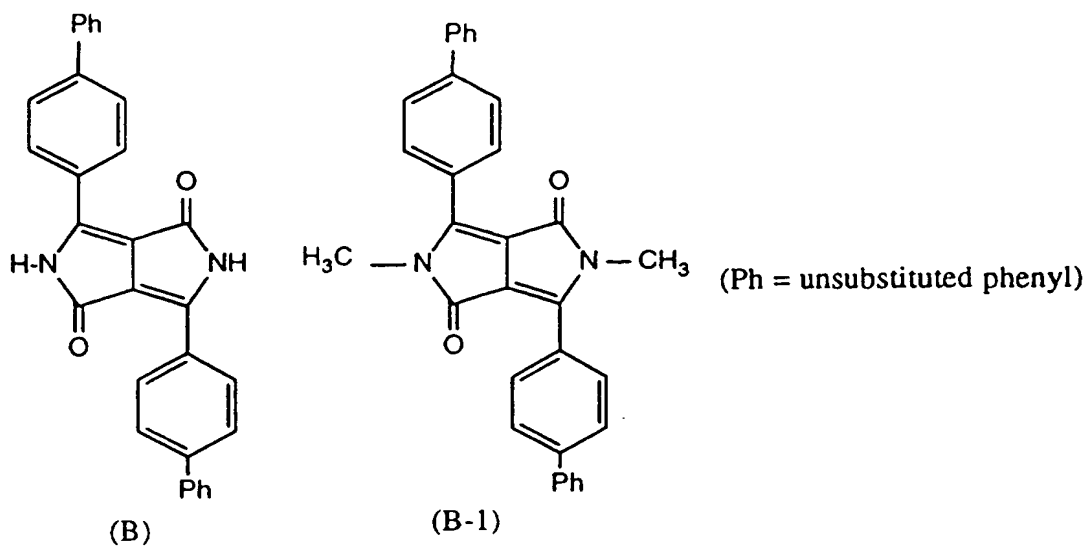
Mass spectrometry (*m/e*): 316 (*M*⁺, 100 %).

Elemental analysis (%): C, 75.94; H, 5.06; N, 8.86 (calculated) and C, 75.88; H, 5.36; N, 8.62 (observed).

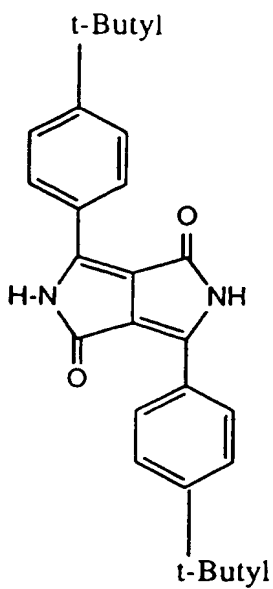
Example 3

Reaction and separation are carried out similarly to Example 1 except that p-diphenyl-1,4-diketo-pyrrolo[3,4-*c*]-pyrrole (indicated by B below) is used instead of 1,4-diketo-pyrrolo[3,4-*c*]-pyrrole, reaction time is prolonged to 72 hours and a solvent mixture consisting of 98 vol% dichloromethane and 2 vol% ethyl acetate is used for the column separation. Analyses reveal that N,N'-dimethyl-p-diphenyl-1,4-diketo-pyrrolo[3,4-*c*]-pyrrole as indicated by B-1 is obtained in a yield of 13 %.

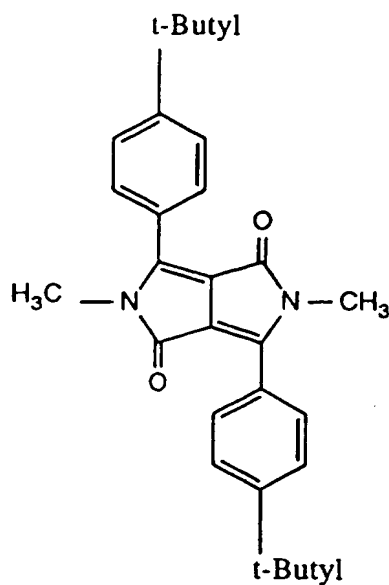
- 11 -

**Example 4**

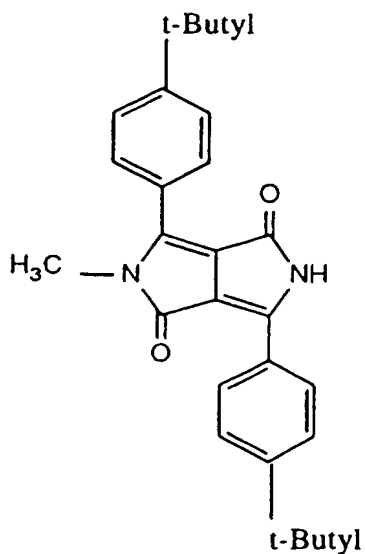
Reaction and separation are carried out similarly to Example 1 except that di-p-tert-butyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole (indicated by C below) is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole and a solvent mixture consisting of 50 vol% dichloromethane and 50 vol% ethyl acetate is used for the column separation. Analyses reveal that N,N'-dimethyl-di-p-tert-butyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole (indicated by C-1) and N-methyl-di-p-tert-butyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole (indicated by C-2) are obtained in yields of 76 % and 6.5 %, respectively.



(C)



(C-1)



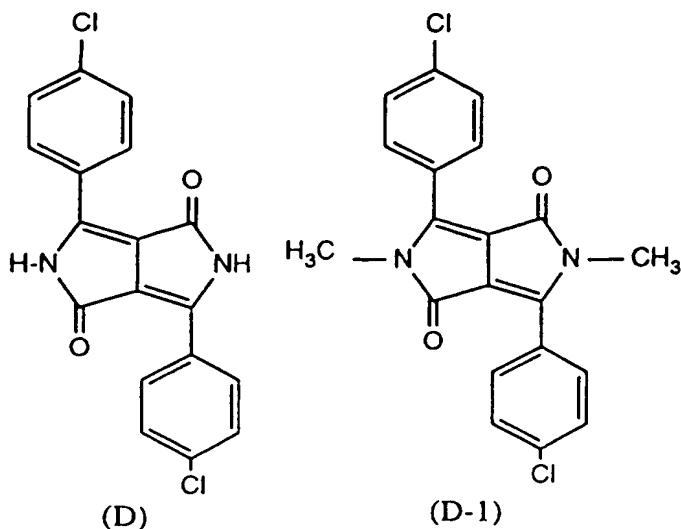
(C-2)

Example 5

Reaction and separation are carried out similarly to Example 1 except that di-p-chloro-1,4-diketo-pyrrolo[3,4-c]-pyrrole (indicated by D below) is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole and a solvent mixture consisting of 50 % dichloromethane and 50 % ethyl acetate is used for the column separation. Analyses reveal that N,N'-dimethyl-di-p-chloro-1,4-diketo-pyrrolo[3,4-c]-pyrrole (indicated by D-1

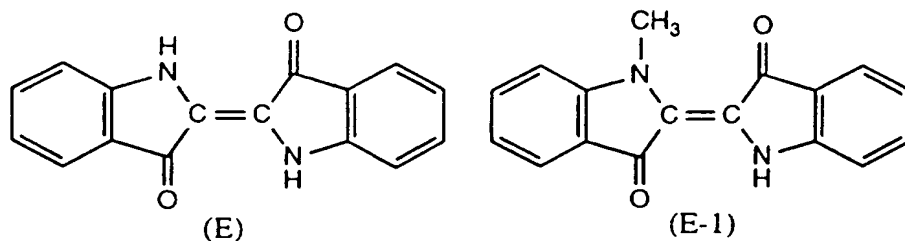
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below) is obtained in a yield of 16 %.



Example 6

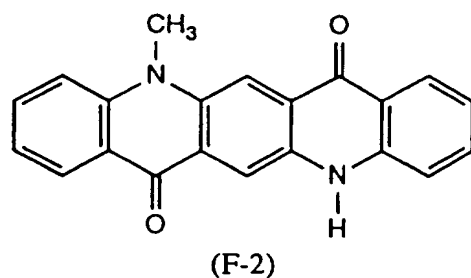
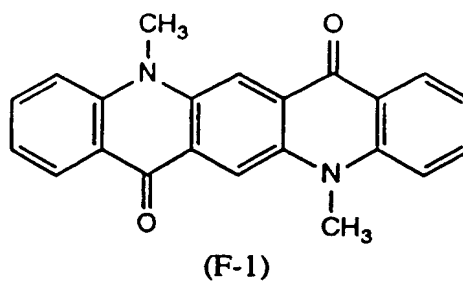
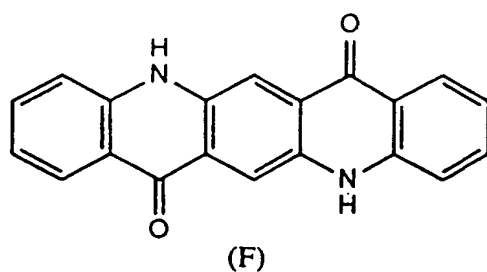
Reaction and separation are carried out similarly to Example 1 except that indigo as indicated by E below is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole, the reaction time is prolonged to 72 hours and dichloromethane is used for the column separation. Analyses reveal that N-methyl-indigo as indicated by E-1 is obtained in a yield of 7 %.



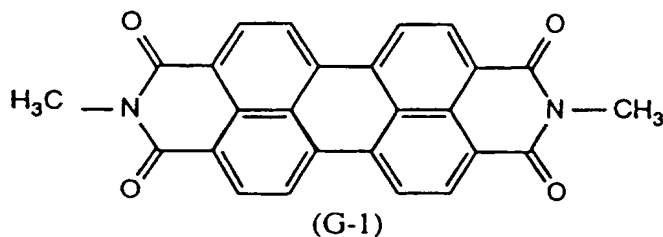
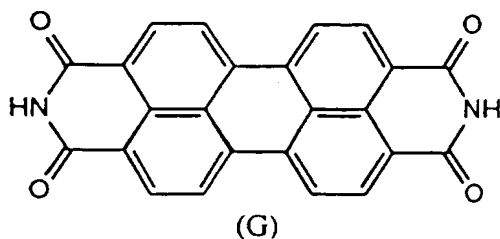
Example 7

Reaction and separation are carried out similarly to Example 1 except that quinacridone as indicated by F below is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole and the reaction time is prolonged to 72 hours. Analyses reveal that N,N'-dimethyl-quinacridone (indicated by F-1) and N-methyl-quinacridone (indicated by F-2) are obtained respectively in yields of 54 % and 42 %.

- 14 -

**Example 8**

Reaction and separation are carried out similarly to Example 1 except that perylenediimide as indicated by G below is used instead of 1,4-diketo-pyrrolo[3,4-c]pyrrole and the reaction time is prolonged to 96 hours. Analyses reveal that N,N'-dimethyl-perylenediimide (indicated by G-1) is obtained in a yield of 62 %.

**Example 9**

Reaction and purification are carried out similarly to Example 2 except that quinacridone is used instead of 1,4-diketo-pyrrolo[3,4-c]pyrrole and the reaction time is shortened to

72 hours. N,N'-dimethyl-quinacridone is obtained in a yield of 92 %.

Example 10

Reaction and purification are carried out similarly to Example 2 except that perylenediimide is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole.

N,N'-dimethyl-perylenediimide is obtained in a yield of 82 %.

What is claimed is:

1. A process for producing an organic pigment represented by general formula



characterized in that an organic pigment represented by formula



is reacted with dimethylcarbonate in the presence of a base with or without a solvent, wherein in formulae I and II $x + y$ is an integer 1 to 4 with x being 0 to 4 and y being 1 to 4, A is the residue of an organic pigment containing $x + y$ cyclic or open $-NH-$ groups, and the H as well as CH_3 in formula I and II are bound to the above mentioned N .

2. A process according to claim 1, wherein $x + y$ is 1 or 2.
3. A process according to claim 1, wherein A in formulae I and II is preferably the residue of a pigment selected from the group consisting of the quinacridone, anthraquinone, perylene, indigo, quinophthalone, isoindolinone, isoindoline, dioxazine, diketopyrrolopyrrole, phthalocyanine or azo-series.
4. A process according to claim 1, wherein the base is one selected from the group consisting of alkaline metals, alkaline metal hydroxides, alkaline metal carbonates, alkaline metal amides, alkaline metal hydrides, alkaline earth metal or alkaline metal alcoholates, which are derived especially from primary, secondary or tertiary aliphatic alcohols with 1 to 10 C-atoms, and organic aliphatic, aromatic or heterocyclic N-bases, or a mixture of at least two thereof.
5. A process according to claim 1, wherein the base is selected from the group consisting of organic aliphatic, aromatic or heterocyclic N-bases, or a mixture of at least two thereof.
6. A process according to claim 1, wherein the base is trimethylamine, triethylamine, pyridine or 4-dimethylaminopyridine, or a mixture of at least two thereof.
7. A process according to claim 1, wherein the reaction is carried out in a solvent.

- 17 -

8. A process according to claim 7, wherein the solvent is a polar organic solvent or a mixture of at least two polar organic solvents.
9. A process according to claim 7, wherein the solvent is tetrahydrofuran, N,N-dimethylformamide, dioxane, dimethylsulfoxide, N,N-dimethylacetamide or N-methylpyrrolidone, or a mixture of at least two thereof.
10. A process according to claim 1, wherein the compound of formula II, the base and dimethylcarbonate are reacted in a molar ratio of 1 : 0.1-1000 : 1-100000, preferably 1 : 1-100 : 10-10000, more preferably 1 : 1-50 : 10-1000 and most preferably 1 : 1-10 : 10-500 for the case where no solvent is used.
11. A process according to claim 1, wherein the compound of formula II, the base and dimethylcarbonate are used in a molar ratio of molar ratio is 1 : 0.1-100 : 0.1-100, preferably 1 : 1-50 : 1-50, more preferably 1 : 1-20 : 1-20 and most preferably 1 : 1-10 : 1-10, and the solvent is used such that the concentration of the compound of formula II is 0.00001-100 mol/l, preferably 0.001-10 mol/l, more preferably 0.01-1 mol/l and most preferably 0.05-0.5 mol/l.
12. A process according to claim 1, wherein the reaction is carried out in an inert atmosphere.
13. A process according to claim 1, wherein the reaction is carried out at a temperature of preferably 30-250°C, more preferably 50-200°C and most preferred 80-150°C.

INTERNATIONAL SEARCH REPORT

In: aonal Application No
PCT/EP 95/03462

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09B67/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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A	EP,A,0 133 156 (CIBA-GEIGY AG) 13 February 1985 see page 10, line 11 - line 13; examples 1A,2,4-6 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 18 no. 313 (C-1212) [6653] ,15 June 1994 & JP,A,06 065510 (NIPPON KAYAKU CO. LTD.) 8 March 1994, see abstract --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Int. onal Application No
PCT/EP 95/03462

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A	SYNTHESIS, no. 5, May 1986 STUTTGART DE, pages 382-383, M. LISSEL ET. AL. 'Dimethylcarbonat als Methylierungsmittel unter phasentransfer-katalytischen Bedingungen' cited in the application see page 382, column 2, line 14 - page 383, column 1 ---	1
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